A new class of cationic iridium(III) complexes of the form \([\text{IC N}]_2\text{Ir-}(\text{N N})\text{[PF}_6\text{]}\) is reported, where \(\text{C N} = \) cyclometallating 2-phenylpyridinato, ppy, or 2-(2,4-difluorophenyl)-5'-methylpyridinato, dFMeppy, and \(\text{N N} = \) guanidyl-pyridine, gpy, or -pyrazine, gpz, as the ancillary ligand. A large blue-shift in the emission coupled with a 7-to-9 fold enhancement in photoluminescence quantum yield and microsecond emission lifetimes were observed for the complexes containing the partially saturated gpy ligand as compared to the benchmark complex \([\text{ppy}]{_2}\text{Ir(bpy)}\text{[PF}_6\text{]}\), \(\text{C1}\), where \(\text{ppy} = 2,2'\text{-bipyridine.}\)

Cationic iridium(III) complexes are the subject of tremendous recent interest due to their use as photoactively active materials in a wide assortment of applications, \(e.g.,\) lighting devices,\(^1\) solar energy harvesters,\(^2\) in sensing or bioimaging\(^3\) and photosensitizers for hydrogen production from water.\(^4\) Generally, the photophysical properties of these complexes can be finely tuned through concomitant modification of the cyclometallating and ancillary ligands. In particular, replacing the 2,2'-bipyridine (bpy) in the archetypal \([\text{ppy}_2]\text{Ir(bpy)}\text{[PF}_6\text{]}\), \(\text{C1}\), with other bidentate heterocyclic ligands has proven to be very effective in modulating the emission energy (ppy = 2-phenylpyridinato). For instance, complexes bearing phenanthrolines,\(^5\) imidazoles,\(^6\) 1,2,3-triazoles,\(^7\) tetrazoles,\(^7\) and pyrazoles\(^8\) as the ancillary ligand (Scheme 1) and contrast their photophysical properties to those of \(\text{C1}\). The observed optoelectronic properties align with the density functional theory (DFT) and time-dependant DFT (TD-DFT) studies \((\text{vide infra})\).

The gpy and gpz ligands were synthesized in high yields \((95\% \text{ and } 82\%)\) according to the literature.\(^6\) These ligands were

\(^{a}\) Département de Chimie, Université de Montréal, 2900 Edouard-Montpetit, Montréal, Québec H3T-1J4, Canada. E-mail: garry.hanan@umontreal.ca; Fax: +1 514 343-2468; Tel: +1 514 343-7056

\(^{b}\) Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK.

\(^{†}\) Electronic supplementary information (ESI) available. CCDC 1015124. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc04069h

\(\text{Scheme 1 Syntheses of 1–3 (a) i. 2.1 equiv. gpy in DCM/MeOH (1:1), 50 °C, 19 h; ii. NH}_3\text{PF}_6\text{(aq). (b) i. 2.1 equiv. gpz in DCM/MeOH (1:1), 50 °C,19 h; ii. NH}_3\text{PF}_6\text{(aq).}\)
used to cleave \([ppy)_2Ir[μ-Cl]_2\) and \([dFMeppy)_2Ir[μ-Cl]_2\) (dFMeppy = 2-(2,4-difluorophenyl)-5-methylpyridinato) and complexes 1–3 were obtained in high yield (80–90%) following an anion metathesis with \(aq. NH_4PF_6\) (Scheme 1). They were fully characterized by \(^1H-, ^13C-, ^19F-NMR\) spectroscopy, melting point and HR-MS analyses (Fig. S1–S11 in ESI†). Resonances in the \(^1H\) NMR spectra of 1–3 corresponding to the saturated aliphatic backbone of the ancillary ligand were observed between 1 to 4 ppm as found in other complexes with saturated ligands. The splitting of the methylene protons suggest that they are diastereotopic as also observed for analogous Ru complexes.6b–e

Crystals of 3 suitable for X-ray structural determination were grown by slow evaporation from a mixture of DCM and disopropylether (1:1, \(v/v\)) (Fig. 1). Selected crystallographic parameters are tabulated in Table S1 (ESI†). Selected bond distances and angles are in Table S2 (ESI†). The \(^1\)Ir[\(μ\)-ion is coordinatively saturated and in a distorted octahedral geometry. The C\(\equiv\)N carbon atoms are found to be mutually cis disposed, similar to the solid-state structure of \(C_1\) (CCDC 745138).9 The average Ir–C\(ppy\) (2.005(10) Å) and Ir–N\(ppy\) (2.054(8) Å) bond lengths are similar to those in \(C_1\) [Ir–C\(ppy\) (2.013(3) Å); Ir–N\(ppy\) (2.045(3) Å)]. The \(N_N\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·

The UV-visible absorption spectra of 1–3 are shown in Fig. S12 (ESI†) and calculated molar absorptivities are reported in Table S3 (ESI†). The absorption profiles are similar to other heteroleptic cationic iridium(III) complexes reported in the literature.10 TD-DFT studies assign the bands below 300 nm to the trend observed with \([(bpy)_2Ru(gpy/gpz)]^2+\) with \(aq. NH_4PF_6\) (Scheme 1). They were fully characterized by \(^1H-, ^13C-, ^19F-NMR\) spectroscopy, melting point and HR-MS analyses (Fig. S1–S11 in ESI†). Resonances in the \(^1H\) NMR spectra of 1–3 corresponding to the saturated aliphatic backbone of the ancillary ligand were observed between 1 to 4 ppm as found in other complexes with saturated ligands.8 The splitting of the methylene protons suggest that they are diastereotopic as also observed for analogous Ru complexes.

The electrochemical behaviour of 1–3 was monitored by cyclic voltammetry (CV) and the CV traces in deaerated MeCN containing 0.1 M \(n\)-Bu$_4$NPF$_6$ as the supporting electrolyte and using Fe/Fe$^+$ as an internal standard at 298 K are shown in Fig. S13 and S14 (ESI†). The detailed CV data vs. SCE (Fc/Fc$^+$ = 0.38 V in MeCN) are summarized in Table S4 (ESI†) while only first redox potentials are listed in Table 1. In the anodic scan, all of the complexes showed three successive oxidation waves, the first quasi-reversible and the other two irreversible. The first oxidation wave of 1–3 falls between 0.99 to 1.21 V (Fig. S14, ESI†) and is assigned to the Ir$^{III/IV}$ redox couple with contributions from the C\(\equiv\)N ligands.5c These oxidation potentials are cathodically shifted to a significant extent compared to other heteroleptic iridium(III) cationic complexes bearing similar C\(\equiv\)N ligands, (C1: $E^{1/2}_o$ = 1.27 V vs. SCE; [dFMeppy)Ir(bpy)]PF$_6$, C2: $E^{1/2}_o$ = 1.35 V vs. SCE). Indeed, DFT calculations show that the HOMOs of 1–3 are constituted almost equally with iridium and the C\(\equiv\)N ligands with a progressive increase in the calculated energy of the HOMO of 2 ($\Delta E_{HOMO} = −5.66$ eV) to 3 ($\Delta E_{HOMO} = −5.43$ eV) to 1 ($\Delta E_{HOMO} = −5.32$ eV), which is in excellent agreement with experiment. The first oxidation potential of 2 ($E^{1/2}_o$ = 1.21 V) is more positive compared to that of 1 ($E^{1/2}_o$ = 0.99 V) due to the electron withdrawing fluorine atoms on the C\(\equiv\)N ligands, which increase the stability of HOMOs. The $E^{1/2}_o$ of 3 is slightly more positive (1.04 V) compared to that of 1, although both contain the same cyclometallating ppy ligand. This is due to
modulating influence of the less electron-donating gpz ligand. Overall, the trends observed in the electrochemistry are entirely consistent with those in the electronic spectroscopy.

Upon scanning to negative potential, 1 and 2 show three successive one-electron irreversible reduction-waves whereas complex 3 shows a first quasi-reversive one-electron reduction followed by two irreversible one-electron reduction events (Fig. S13 and Table S4, ESI†). The first of the reduction waves falls between −2.12 to −1.60 V, which are more cathodically shifted compared to benchmark complexes C1 and C2 (C1: \( E_{1/2} = -1.38 \) V; C2: \( E_{1/2} = -1.34 \) V). The more negative reduction potentials in 1–3 are the result of the strongly electron-donating guanidyl moiety. Similar effects were previously observed for more electron rich ancillary ligands (N \(_4\) guanidyl moiety). Similar effects were previously observed for N \(_4\) guanidyl moiety. Similar effects were previously observed for

<table>
<thead>
<tr>
<th>( \lambda_{em}/nm )</th>
<th>( \Phi_{pl}/% )</th>
<th>( \tau_e/\mu s )</th>
<th>( k_{nr}/10^5 ) s(^{-1} )</th>
<th>( E_{1/2}^{pa} ) (^+) V</th>
<th>( k_{nr}/10^5 ) s(^{-1} )</th>
<th>( E_{1/2}^{pa} ) (^+) V</th>
<th>( k_{nr}/10^5 ) s(^{-1} )</th>
<th>( E_{1/2}^{pa} ) (^+) V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>503</td>
<td>60</td>
<td>2.1</td>
<td>2.9</td>
<td>1.9</td>
<td>0.99 (88)</td>
<td>-2.13</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>470, 498</td>
<td>62</td>
<td>2.6</td>
<td>2.3</td>
<td>1.4</td>
<td>1.21 (72)</td>
<td>-2.12</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>640</td>
<td>0.2</td>
<td>0.02</td>
<td>1.0</td>
<td>499</td>
<td>1.04 (92)</td>
<td>-1.60 (95)</td>
<td></td>
</tr>
</tbody>
</table>

* \( \Phi_{pl} \) was measured at 298 K using quinine sulfate (\( \Phi_{pl} = 54/\% \), in 0.5 N H\(_2\)SO\(_4\)) as in ref. 16. \( k_{nr} = (1 - \Phi_{pl}\)/\( \Phi_{pl}\) \( \times \) \( k_{nr} \)). CV values are in V vs. SCE. \( \Delta E_{pa} = [E_{pa} - E_{pc}] \), where \( E_{pa} \) = anodic peak potential and \( E_{pc} \) = cathodic peak potential; \( E_{1/2} = (E_{pa} + E_{pc})/2 \) and result from one-electron processes. A non-aqueous Ag/Ag\(^+\) electrode (silver wire in a solution of 0.1 M AgNO\(_3\) in MeCN) was used as the pseudoreference electrode; a glassy-carbon electrode was used for the working electrode and a Pt electrode was used as the counter electrode.

corrobore these assignments. The CT emission in 1 is the result of mixed LLCT and MLCT that is mostly LLCT in nature and involves the pyridine moieties of the C–N ligands while the CT emission of 3 is also mixed with almost equal LLCT and MLCT contributions that involve the pyrazine of the gpz ligand. The emission maximum of 3 is at 640 nm, which is significantly red-shifted as compared to those of 1 and 2. With the presence of the dFMeppy ligand, the emission maximum in 2 is expectedly blue-shifted to 470 nm. Consistent with the absorption and electrochemical data, the emission maxima for 1 and 2 are hypsochromically shifted as compared to those of C1 (\( \lambda_{em} = 602 \) nm) and C2 (\( \lambda_{em} = 527 \) nm). This effect is again due to the strong \( \sigma \)-donating nature of the guanidyl moiety that destabilizes both the HOMO and LUMO, the latter to a greater extent resulting in a larger HOMO–LUMO gap. In the case of 3, the LUMO now resides on the guanidine-based ligand, which is significantly lower in energy due to the electron-deficient pyrazine moiety.

The photoluminescence quantum yields, \( \Phi_{pl} \), in degassed MeCN for 1 and 2 are ca. 61%. Complex 3, by contrast is very poorly emissive (\( \Phi_{pl} = 0.2/\% \)) due to a two-order increase in the non-radiative decay rate constant, \( k_{nr} \). The inference is that implicating the pyrazine-based ancillary ligand in the triplet state results in quenched emission. Emission lifetimes for 1 and 2 are 2.1 and 2.6 \( \mu s \), respectively, and are significantly longer than that of C1 (\( \tau_e = 0.275 \) \( \mu s \)) while the \( \tau_e \) of 3 is only 20 ns. The conformational flexibility present in the saturated backbone of the guanidyl cycle coupled with a triplet state involving the pyrazine moiety, may be responsible for the short observed lifetime in 3. Indeed, very efficient vibrational deactivation was previously noted for Ru(II) complexes of guanidine-based ligands.\(^{15}\)

In summary, a new class of blue-green emissive iridium(III) cationic complexes with partially saturated guanidyl-containing ancillary ligands is reported. The strong electron-donating character of the guanidyl cycle confers a very large blue shift in the emission compared to benchmark complex C1 while maintaining high photoluminescence quantum yields and microsecond emission lifetimes. Incorporation of a pyrazine unit in 3 results in near complete quenching of the luminescence with a concomitant red-shift of its emission wavelength.
The overall structural, electrochemical and photophysical properties of 1 and 2 are encouraging and current efforts are underway to investigate these complexes as emissive materials in solid-state lighting applications.

The authors are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Fonds québécois de la recherche sur la nature et les technologies (FRQNT), the Centre for Self Assembled Chemical Structures (CSACS), the Centre in Green Chemistry and Catalysis (CCVC), and the University de Montréal (UdeM) for financial support. UdeM is also thanked. EZ-C acknowledges the University of St Andrews for financial support.

Notes and references


11 For overlay of experimental absorption spectra of the complexes in acetonitrile with their predicted transitions and oscillator strength, see Fig. S14–S16, ESI†.


